ELECTROCHEMICAL ETCHING OF SHAPE MEMORY ALLOY USING NEW ELECTROLYTE SOLUTIONS

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ABSTRACT

This paper presents electrochemical etching characteristics of shape memory alloy (SMA) using new electrolytes of inorganic salt in alcohol, in comparison with conventional H_2SO_4-methanol solution. Pattern etching of SMA sheets could be carried out in the electrolyte solutions using LiCl and NH_4Cl. Especially in the case of the 1mol/l LiCl -ethanol, good etching properties such as controllable low etch rate, uniform etching depth and flat etched surface were obtained. The etch factor (= etching depth / side etching width) was 1.5 in 1mol/l LiCl-ethanol and 2.0 in 0.1mol/l LiCl-ethanol. Throughout etching could be carried out by using a backside dummy metal. This etching technique has been applied to the micromachining of SMA sheet and SMA pipe for fabrication of actuators.

INTRODUCTION

Electrochemical etching i one of the most suitable methods for the micromachining of NiTi SMA [1-4]. Batch fabrication process is more favorable in mass-productivity than individual drawing methods such as a laser cutting for fabrication of complex microstructures. As compared with conventional chemical etching, the electrochemical etching has features of high etching rate and low side etching [2,3]. Only the solution of 5vol% (about 1mol/l) H_2SO_4 -methanol has been reported for an electrolyte of the electrochemical etching of SMA, including our previou work [1-4]. The etching rate is over 10µm/min, however, controllable low etching rate is required for precision machining of thin SMA materials. It is difficult to depress the etching rate using conventional H_2SO_4-methanol solution, because the etching tends to proceed non-uniformly like worm-eaten shape under low etching rate conditions such as low applied voltage and low electrolyte concentration [3].

The electrolyte of the H_2SO_4 is very reactive with the methanol, therefore, it is difficult to prepare the mixed H_2SO_4-methanol solution. The mutual reactivity also influences on stability of the mixed solution. Fresh solution is necessary for effective etching [1]. The solution has also problems that it is corrosive and toxic. Although it is troublesome to use the solution, no other solutions have been s tudied up to the present. Non-corrosive, non-toxic and stable electrolyte solution is required for industrial applications.

In this work, safety inorganic salts of NH_4Cl, $NaClO_4$ and LiCl, that have high solubility with alcohol solvents [5], were selected for electrolyte. Basic characteristics of the electrochemical etching of SMA sheets have been studied in comparison with the conventional H_2SO_4 -methanol, especially from the viewpoint of the depression of the etching rate.

The electrochemical etching techniques using new electrolytes have been applied to fabrication of actuators from an SMA sheet and an SMA pipe.

EXPERIMENTAL

To prepare non-aqueous electrolyte solution , H_2SO_4, NH_4Cl, $NaClO_4$ or LiCl was dissolve in methanol or ethanol.

Electrochemical etching was carried out in a setup shown in Fig.1. DC voltage was applied between the SMA anode (about 20×15mm^2) and the counter cathode of a stainless steel plate (50×50mm^2). Both electrode were facing each other with a gap of 40mm.

Cold-rolled SMA sheets of 51%NiTi were used for etching. After the oxide film on the surface was removed by hydrofluoric and nitric acid, negative photoresist pattern (OMR83 Tokyo Ohka Kogyo Co., ltd.) was formed for the etching mask. Thickness of the resist was about 1.5 μ m.

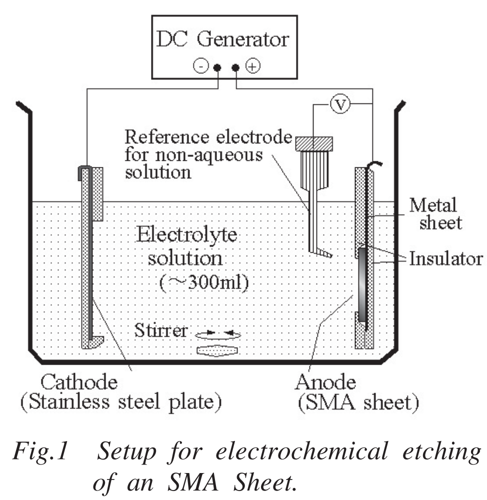


Fig.1 Setup for electrochemical etching of an SMA Sheet.

RESULTS AND DISCUSSION

Current-voltage Characteristics

For a previous experiment to study electrochemical behavior, electrolytic current-voltage curves in various electrolytes were measured. Open area of the SMA surface of 5 ×5mm^2 was in contact with the solution. The applied voltage almost contributed to the potential of the SMA electrode because the counter electrode wa large enough [3]. Results of the measurements are shown in Fig.2.

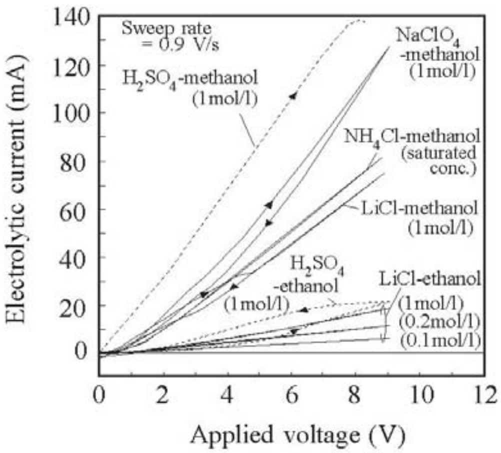


Fig.2 Current-voltage curves of electrochemical etching of SMA in various solutions.

Electrolytic currents were obtained using NH $_4$Cl, NaClO$_4$ and LiCl electrolytes in addition to conventional H_2SO_4. Current-voltage curves have no large hysteresis except H_2SO_4-ethanol. It suggests that the currents are caused by dissolution of the SMA and there are no influences from other electrochemical reactions such as surface oxidation.

The current with ethanol tends to be much lower than that of methanol. It seems that the solutes tend to be less ionized in ethanol than in methanol because the polarization of ethanol is lower than that of methanol.

Pattern Etching

Meandering patterns that consist of 60/20μm line/space was used for etching. Etching rate, etch factor and etched shape were evaluated, when the SMA sheet wa half-etched about 2 μ m in depth under various electrolytic conditions. Etching conditions and the results are summarized in Table 1.

Electrolytic currents during the pattern etching were also measured. The etch rate in the Table 1 is approximately proportional to the averaged currents during the etching under all conditions. Current densities were slightly les than that of the current -voltage curve (Fig.2), because of the influence of the narrow etching pattern.

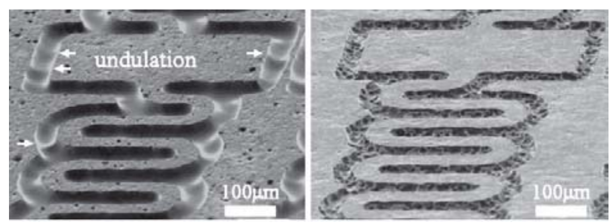
SEM photographs of the etched SMA sheets are shown in Fig.3.

Table 1 Results of electrochemical etching in various electrolytes.

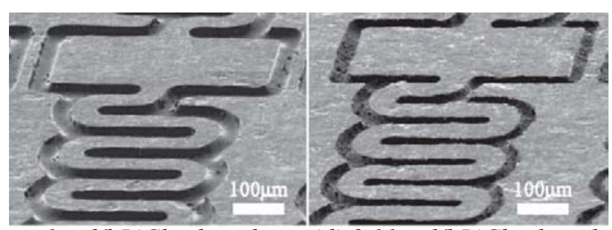
Solute	Solvent	Conc. (mol/l)	Applied voltage (V)	Etching rate (•m/min)	Etch factor	Etched surface
H_2SO_4	methanol	1.0	8	16	1.5	smooth (undulate)
H_2SO_4	ethanol	1.0	8	2.7	~1.5	extremely rough
LiCl	ethanol	1.0	8	3.5	1.5	smooth
LiCl	ethanol	0.1	8	1.8	2.0	rough
LiCl	methanol	1.0	8	12	1.5	smooth
NH_4Cl	methanol	<0.2	8	10	1.5	rough
$NaClO_4$	methanol	1.00	8	(Resist NG)		

In the conventional electrolyte of 1mol/l H_2SO_4 -methanol, etching rate of 16μm/min and etch factor of 1.5 were obtained at an applied voltage of 8V. Mirror like etched surface was obtained. The bottom surface of the etched grooves was undulating locally as shown in Fig.3(a). The undulations are unfavorable for precise micromachining.

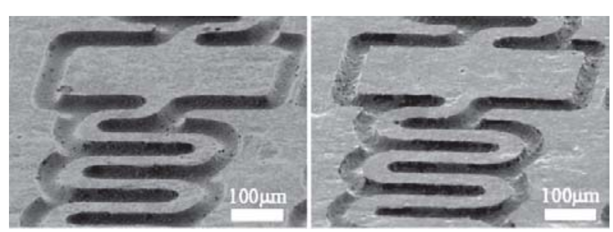
In the case of H_2SO_4-ethanol, etching rate could be depressed to 2.7 μm/min, however, etched surface became extremely rough (Fig.3(b)). Hysteresis in Fig.1 suggests that anodic reaction of etching and passivation proceeded simultaneously.



(a) 1mol/l H_2SO_4-methanol (DC8V, 22μm depth) *(b) 1mol/l H_2SO_4-ethanol (DC8V, 22μm depth)*



(c) 1mol/l LiCl-ethanol (DC8V, 21μm depth) *(d) 0.11mol/l LiCl-ethanol (DC8V, 18μm depth)*



(e) 1mol/l LiCl-methanol (DC8V, 24μm depth) *(f) saturated NH_4Cl-methanol (DC8V, 20μm depth)*

Fig.3 Electrochemically etched SMA sheets.

Good etching with over 1.5 etch factor could be carried out using LiCl electrolyte. It is an essential behavior of the electrochemical etching that the etch factor become over 1.0. According to a numerical simulation of electrolytic current distribution in an etched groove, etch factor should be higher than 1.0. [6].

In the case of 1mol/l LiCl-ethanol, etch factor was a high as 1.5 in spite of the low etch rate of 3.5 µm/min. The etched surface was very flat and without undulation as shown in Fig.3(c). Under low LiCl concentration of 0.1mol/l, the etched surface was slightly rough (Fig.3(d)) however, the etch rate decreased further and the etch factor increased to 2.0. The LiCl in ethanol solution i most suitable for narrow pattern etching with lo etching rate. The solution has another advantages that it is non-corrosive, non-toxic, stable and easy to recycle the LiCl from used solution.

In 1mol/l LiCl-methanol, etching rate was over 10µm/min, however, uniform etching with etch factor of 1.5 could be carried out (Fig.3(e)). In substitution for the conventional 1mol/l H_2SO_4-methanol, LiCl -methanol can be usable for the purpose of high rate etching.

In saturated (<0.2mol/l) NH_4Cl-methanol, etched surfaces were slightly rough, however, etch rate of 10µm/min and etch factor of 1.5 could be obtained (Fig.3(f)). This solution is also usable for rough etching. Although the SMA etching could be carried out in $NaClO_4$-methanol, photoresist patte rn of the etching mask was attacked during the etching because of the oxidation effect of the solution.

Throughout Etching

Throughout etching is very important to make actuators from an SMA sheet. During the over-etching after throughout, the etching tend s to proceed non-uniformly because the electrolytic current distribution becomes non -uniform [3]. In the case of conventional etching, conductive dummy layer of Ni or Cu on the backside of the SMA sheet is very effective to maintain a uniform throughout etching [3,4]. In order to investigate the electrochemical behavior of the metals in new electrolytes solutions, electrolytic current-voltage curves of Ni and Cu were measured as shown in Fig.4. The current-voltage curves of Ni were alike to the curves of th e SMA in all solutions. In LiCl-methanol and LiCl-ethanol, the curves of Cu had large hysteresis, therefore, currents at 8V, that is applied voltage for the SMA etching, were lower than the current of the SMA. It suggests that the electrochemical etching rate of Cu are lower than that of SMA in LiCl-methanol and LiCl-ethanol.

By using electroplated Ni and Cu film as a backside dummy layer, the SMA sheet could be etched throughout uniformly in LiCl-ethanol as shown in Fig.5 and Fig.6. Although Cu surface at the bottom of the etched groove was rough, The Cu has the merit that the electrochemical etching rate was lower than that of the SMA, therefore, thin Cu film is usable for the dummy layer.

Ni and Cu could be removed in concentrated nitric acid without da mage to the SMA surface as shown in Fig.5(b) and Fig.6(b). [3,4]. Removal rate of the Ni and the Cu films were about 0.2 and 3 µm/min, respectively.

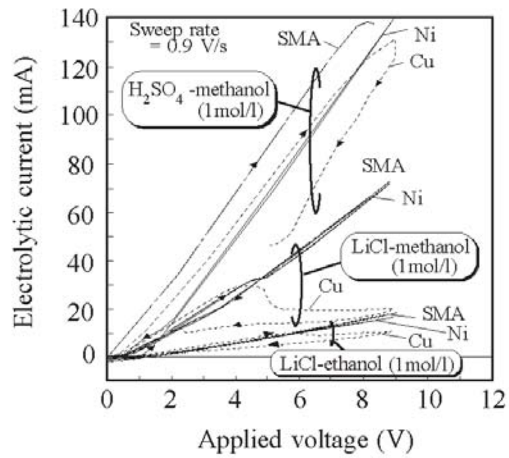
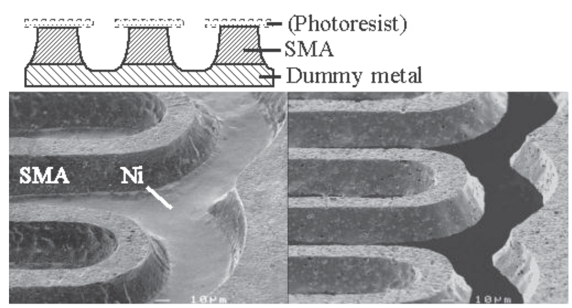
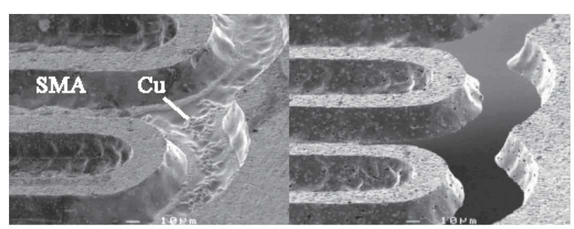


Fig.4 Current-voltage curves of electrochemical etching of dummy metals in various solutions.



(a) Throughout etching (b) Dummy Ni removal
Fig.5 Throughout etching with Ni dummy layer in 1mol/l LiCl-ethanol.



(a) Throughout etching (b) Dummy Ni removal
Fig.6 Throughout etching with Cu dummy layer in 1mol/l LiCl-ethanol.

Application to Actuator Fabrication

Flat meandering shaped SMA actuators were fabricated from an SMA sheet of 30µm in thickness as shown in Fig.7. The SMA sheet was etched through in LiCl-ethanol with the dummy Ni layer . In comparison with the conventional etching, more uniform and precise fabrication could be realized by using the LiCl-ethanol solution.

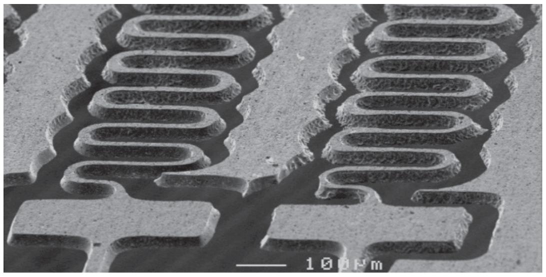


Fig.7 Meandering shape SMA actuators fabricated from an SMA sheet. (in 1mol/l LiCl・Ethanol)

Figure 8 shows an SMA actuator unit for active catheter bending. Three meandering actuators are formed in an SMA pipe. The batch fabrication of the actuator unit in an SMA pipe has a merit to simplify the assembly of active catheter.
The SMA pipe was dip coated with positive photoresist (OFPR800 Tokyo Ohka Kogyo Co., ltd.) of about 5 μ m in thickness. The photoresist was patterned by using projection exposure method for an etching mask. The SMA pipe was electrochemically etched in the LiCl-ethanol solution with a cylindrical surrounding counter electrode as shown in Fig.9. Cu dummy layer was deposited on the inside wall of the pipe by electroless plating previously. It is not easy to deposit thick Cu layer inside the small diameter pipe, however, thin Cu film was enabled to use as the dummy layer in the LiCl-ethanol solution because of the low etching rate of the Cu.

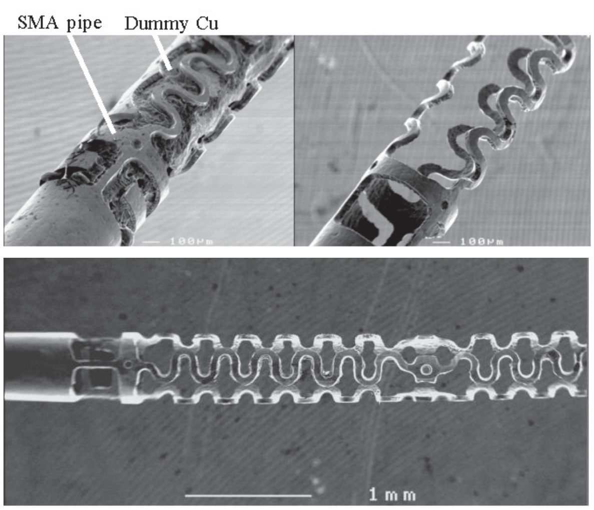


Fig.8 Meandering shape SMA actuators fabricated from an SMA pipe. (in 1mol/l LiCl-ethanol).

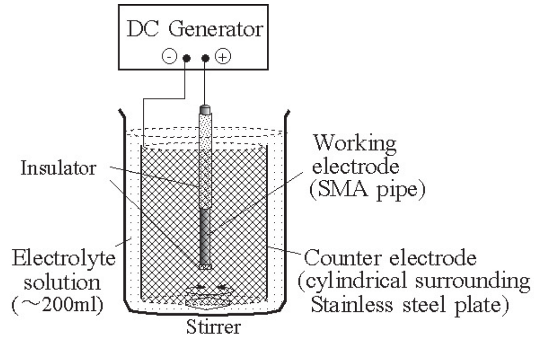


Fig.9 Setup for electrochemical etching of an SMA pipe.

CONCLUSIONS

Basic characteristics of an SMA electrochemical etching in new electrolyte solutions have been studied from the viewpoint of the etching rate depression. Good etching properties such as controllable low etch rate, uniform etching depth and high etch factor could be obtained in LiCl-ethanol. Throughout etching could be carried out uniformly with backside dummy metals of Ni and Cu. Thin Cu film was usable for the electrochemical etching in LiCl -ethanol, because of its low etching rate. This etching technique realized the precise fabrication of micro actuators from a thin SMA sheet and an SMA pipe with small diameter.

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